

# Electrostatic Interaction between Two Charged Gel Layers

N. I. Zharkikh\* and S. S. Dukhin\*\*

\* *Institute of Biocolloid Chemistry, Ukrainian Academy of Sciences, pr. Vernadskogo 42, Kiev, 252680 Ukraine*

\*\* *Dumanskii Institute of Colloid and Water Chemistry, Ukrainian Academy of Sciences, pr. Vernadskogo 42, Kiev, 252680 Ukraine*

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**Abstract** – Analysis of the effect of the distance between two plates with thick gel layers on the Stern potential and disjoining pressure has shown that the interface potential difference inside of the gel layer results in a dependence which should be taken into account when further developing the DLVO theory. Analysis of the electrostatic interaction is based on combining the model of the porous double layer at the oxide–solution interface (first introduced by J. Lyklema) and that of charge regulation. Treatment of the electrostatic interaction involving the extended model of the porous double layer is of particular importance in the study the stability of biocolloids. Cell glycocalyx is permeable for ions; it has considerable thickness and carries a certain amount of ionogenic groups whose degree of dissociation is dependent on the thickness of the electrolyte interlayer and on the potential distribution, thus being varied inside of the gel layer. The extended model of the porous double layer makes it possible to take into account specific electrosurface properties of the biological cells, contrary to the model used by Ohshima, where constancy of the charge is suggested. This fact makes the problem more complicated, since potential is varied across the gel layer and calculation of the charge distribution becomes necessary.

## INTRODUCTION

The universally recognized theory of hydrosol stability, developed by Derjaguin, Landau, Verwey, and Overbeek [1], is closely related to the classical model of the electrical double layer for hydrosols. This model assumes that the particle surface carries charge, concentrated within an infinitely thin layer, and this charge is compensated by the charge distributed over the diffuse plate. The main parameter characterizing the electrical double layer in this model is the surface potential ( $\zeta$ -potential). When all assumptions of this model are fulfilled, the  $\zeta$ -potential may be calculated from electrokinetic measurements, then the value obtained may be employed in the DLVO theory formulas to calculate the electrostatic repulsion between colloidal particles.

Comprehensive study of the electrosurface properties reveals that the classical model of the electrical double layer adequately fits the experimental data for most of the actual colloids, and silver iodide sol above all. However, similar studies of other colloids, in particular, sols of different oxides, demonstrated clearly that the classical model fails to correlate measured values of different effects. The main discrepancy was found to be between very high values of the fixed particle charges and the surface conductance of the particles, on one hand, and between low values of electrophoretic mobility and stability on the other.

Various corrections to the classical model of the electrical double layer have been suggested in order to overcome these difficulties. One of the most useful hypotheses was proposed by Lyklema in 1968 [2]. Lyklema suggested that particles are covered by the gel

layer, where a significant share of the mobile charge of the electrical double layer is concentrated, and only a small share of the net charge of the electrical double layer (the so-called electrokinetic charge) is distributed over the traditional diffuse layer, i.e., over the free solution outside the gel layer. This hypothesis was further developed by various authors [3 - 6], being refined by various corrections and additional assumptions. Major attention, however, was focused by these authors on the analysis of the behavior of the surface charge, and problems of stability have been only slightly touched on within the framework of this model.

Treatment of the electrostatic interaction in terms of the extended model of the porous double layer is of special importance for the analysis of biocolloid stability. Cell glycocalix is permeable for ions; it has considerable thickness and carries a certain amount of ionogenic groups. It may be assumed that due to these features, the extended model of the electrical double layer would result in a better description of the disjoining pressure between biological cells than the classical model.

The analysis of the effect of the gel layer on stability, performed by Ohshima [7] for the interaction of ionite particles with particles of a different nature (including interaction with other ionite particles), was the most adequate. Ohshima considered the case of constant density of a fixed spatial charge, which is typical only for very acidic or very basic ionites. The constancy of a fixed charge is but a specific case of the gel layer models. In general, the charge density is dependent on the electrical double layer potential. This evi-



dence significantly complicates the problem, since it involves variation in the potential inside of gel layer, thus necessitating the relevant calculation of the charge distribution.

The aim of this paper is to describe a general approach to the derivation of the theory of ion-electrostatic interaction of the particles with charged gel layers, and to analyze simple limiting cases of the general formulas.

### SETTING UP A PROBLEM

Disjoining pressure in a slit between two identical planar surfaces (Fig. 1) is equal to the excess osmotic pressure of a solution at the point where solution is not affected by the electric force, i.e., in the center of the slit. When  $N$  types of ions with valence  $z_i$  and concentration  $C_i$  are presented in a solution, then denoting the potential in the center of the interlayer with  $\psi_0$ , we can express the disjoining pressure  $P$  using the following formula:

$$P = RT \sum C_i (e^{-z_i \psi_0} - 1) \quad (1)$$

(from this point on, only dimensionless potential measured in  $RT/F$  units is used; the symbol  $\Sigma$  denotes summation over types of ions from 1 to  $N$ ; index  $i$  indicates a definite type of ions).

The potential profile in a double-layered medium consisting of both the solution interlayer and a sufficiently thick gel layer should be derived in order to calculate  $\psi_0$ . Consider first the boundary conditions of this problem. By denoting the permittivities of the solution and the gel by  $\epsilon_s$  and  $\epsilon_g$ , respectively, we achieve the values

$$\kappa_{s,g} = \sqrt{\frac{4\pi F^2}{RT\epsilon_{s,g}} \sum C_i z_i^2}, \quad (2)$$

which are inverse screening lengths in these media. Coordinate  $x$  is normalized to the screening length in the respective medium:

$$x_s = \kappa_s x; \quad x_g = \kappa_g x.$$

Making use of these notations, the boundary conditions may be written as

$$\left. \frac{d\psi}{dx_s} \right|_{x_s=0} = 0, \quad (3)$$

which is a condition of the symmetry of the potential distribution;

$$\psi|_{x_s=h-0} = \psi|_{x_g=h+0} \quad (4)$$

is a condition of the potential continuity at the phase boundary (if  $X_A$  is the total interlayer width, then

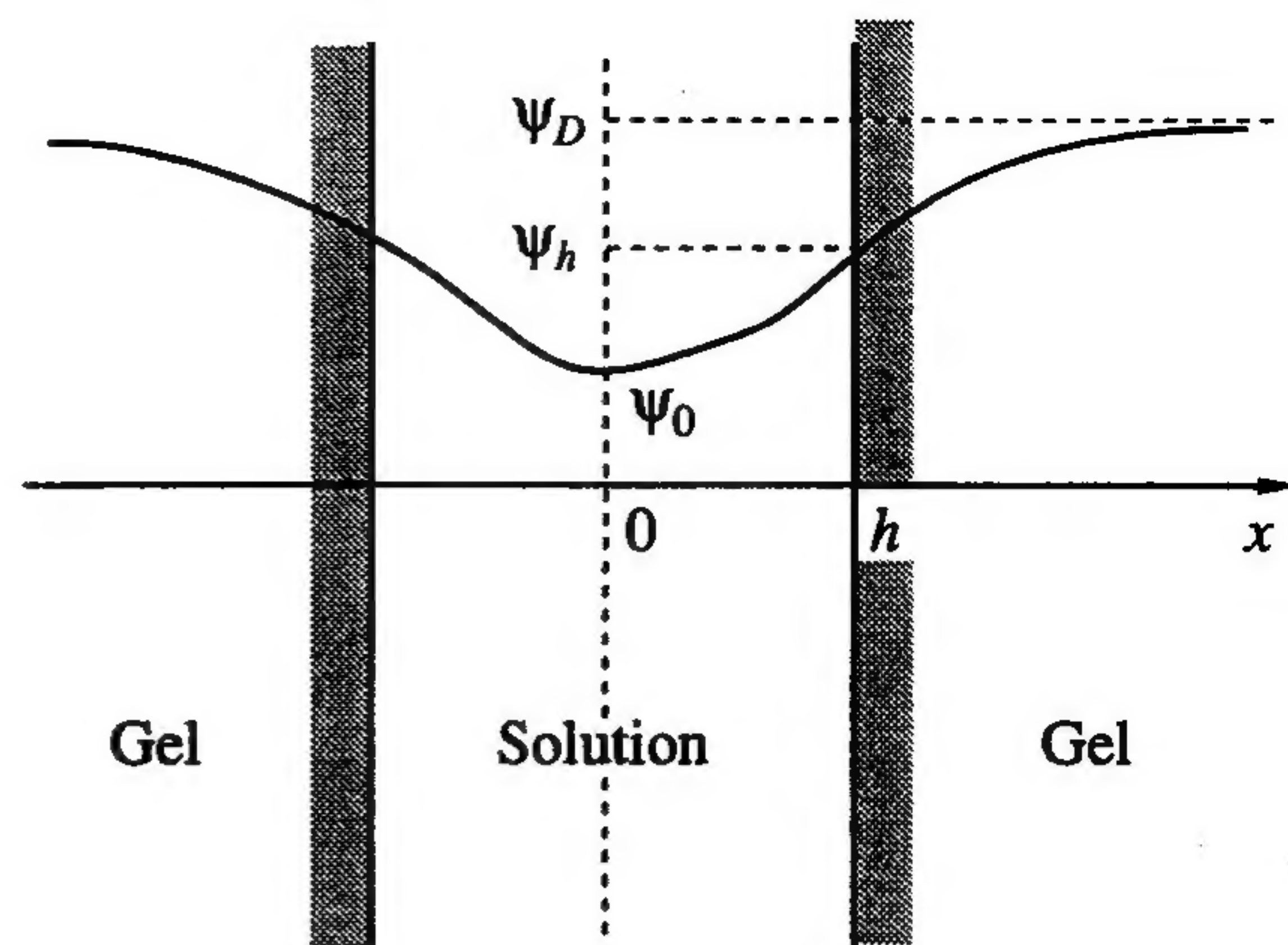


Fig. 1. Coordinate system and notations to figures.

$H = \kappa_s X_A / 2$  is the dimensionless half width of the interlayer);

$$\kappa_s \epsilon_s \left. \frac{d\psi}{dx_s} \right|_{x_s=h-0} = \kappa_g \epsilon_g \left. \frac{d\psi}{dx_g} \right|_{x_g=h+0} \quad (5)$$

a condition of the continuity of the dielectric induction;

$$\left. \frac{d\psi}{dx_g} \right|_{x_g \rightarrow \infty} = 0, \quad (6)$$

and

$$\psi|_{x_g \rightarrow \infty} = \psi_D \quad (7)$$

are conditions of the uniformity of the gel volume;  $\psi_D$  is the potential of the bulk phase of the gel. In the theory of ionites, this value is known as the Donnan potential. This potential is independent of any interlayer properties and is solely determined by the properties of both the gel, and the solution which is in equilibrium with the gel. Since the uniform volume is neutral electrically, the potential  $\psi_D$  may be determined from the equation

$$\rho_g(\psi_D) = 0. \quad (8)$$

A specific expression for gel charge density  $\rho_g$  will be discussed further.

In solution, the potential obeys the Poisson-Boltzmann equation

$$\frac{d^2 \psi}{dx_s^2} = - \sum \lambda_i e^{-z_i \psi}; \quad \lambda_i = \frac{C_i z_i}{\sum C_i z_i^2}. \quad (9)$$

In gel, the ion concentration is not expressed in terms of potential through the Boltzmann distribution; first, the density of active sites and, hence, the maximum ion concentration, are finite; second, ions interact with active sites in a specific way, i.e., not electrostatically. Two variants of distribution are considered most often. The first case represents independent adsorption [4] when there are adsorption potentials  $\Phi_i$  for each type of ion, and site densities  $Q_i$  are attributed strictly to ions of the  $i$ th type. The second case refers to competitive adsorption [5], when net site density is intro-



duced and each single site may be occupied by an ion of any type or remain free. Theoretically, we may also consider any intermediate case which may be a combination of these two variants. A number of problem parameters, related to the ionic components, may range from  $N$ , for competitive adsorption, to  $2 \times N$ , for independent adsorption, respectively. Here, we focus attention on the independent adsorption model. Concentrations of the adsorbed ions  $A_i$  are

$$A_i = C_i \beta_i; \quad \beta_i = \frac{e^{-\Phi_i - z_i \psi}}{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi}}, \quad (10)$$

and the charge density is

$$\rho_g = F \sum z_i A_i. \quad (11)$$

Expression (10) is, in fact, an adsorption isotherm of the Langmuir–Stern type; this distribution is converted to the Boltzmann distribution at  $\Phi_i = 0$  (no specific interaction between ions and gel) and  $Q_i \rightarrow \infty$  (no saturation). Potential within the gel layer obeys the Poisson equation where charge density is expressed by formula (11):

$$\frac{d^2 \psi}{dx_g^2} = - \sum \lambda_i \beta_i. \quad (12)$$

In compliance with [2], this equation will be referred to as the Poisson–Langmuir equation.

### GENERAL SOLUTION

Since the right-hand terms of equations (9) and (12) are dependent solely on the unknown function, one may readily obtain the general solution of these equations in quadratures. Single integration of the equation (9) with account for (3) yields the following solution:

$$\left( \frac{d\psi}{dx_g} \right)^2 = 2 \sum \frac{\lambda_i}{z_i} (e^{-z_i \psi} - e^{-z_i \psi_0}). \quad (13)$$

Double integration of equation (13) gives

$$h = \int_{\psi_0}^{\psi_h} \frac{d\psi}{\sqrt{2 \sum \frac{\lambda_i}{z_i} (e^{-z_i \psi} - e^{-z_i \psi_0})}}. \quad (14)$$

For the potential  $\psi_D$ , we transform equation (8) to the following form:

$$\sum \lambda_i \frac{e^{-\Phi_i - z_i \psi_D}}{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_D}} = 0. \quad (15)$$

The single integration of equation (12), with account for equations (6) and (7), yields

$$\left( \frac{d\psi}{dx_g} \right)^2 = 2 \sum v_i \ln \left[ \frac{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_h}}{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_D}} \right]; \quad (16)$$

$$v_i = \frac{Q_i}{\sum C_i z_i^2}.$$

Inserting equations (10) and (16) into (5), we get

$$\epsilon_s \sum \frac{\lambda_i}{z_i} (e^{-z_i \psi_h} - e^{-z_i \psi_0}) = \epsilon_g \sum v_i \ln \left[ \frac{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_h}}{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_D}} \right]. \quad (17)$$

Having calculated  $\psi_D$  by solving equation (15), we substitute the resultant expression into equation (17). Then equations (14) and (17) form a system of two transcendental equations needed to calculate  $\psi_h$  and  $\psi_0$ .

Maximal disjoining pressure in our case is achieved at surface contact, i.e. at  $h \rightarrow 0$ . As seen from (14), in this case  $\psi_0 \rightarrow \psi_h$ , i.e., the potential inside a very thin layer remains constant. Substituting  $\psi_0 = \psi_h$  into equation (17), we obtain the solution of this equation:

$$\psi_h = \psi_D. \quad (18)$$

Furthermore, inserting equation (8) into (1), we get

$$P_{\max} = RT \sum C_i (e^{-z_i \psi_D} - 1). \quad (19)$$

This expression is valid for the considered case of infinite gel layers, as well as for the interaction of gel layers of arbitrary thickness. Indeed, since at the coalescence of two gel layers a spatially uniform phase is formed, the potential of this phase is bound to take the value  $\psi_D$ , which is independent of geometrical parameters of the phase, such as its thickness.

The fundamental importance of formula (19) is that it indicates the quantitative difference between the behavior of the particles, with and without the gel layer. The electrostatic component of the disjoining pressure for the particles without gel layers is solely governed by the surface potential, whereas for the particles with gel layers the controlling factor is potential  $\psi_D$ , which is always higher than the surface potential. Since any complete description of the particles with gel layers requires knowledge of potential  $\psi_D$ , a measurement of only  $\zeta$ -potential cannot provide all the necessary information.

### LOW POTENTIAL DIFFERENCE

Hence, the potential difference between the depth of the gel layer and the middle of the infinitesimal thickness interlayer is lacking. Therefore, at small thick-



nesses this difference is small. We take advantage of this fact to obtain an approximate solution. We denote

$$\Delta\psi_1 = \psi_D - \psi_h; \quad \Delta\psi_2 = \psi_h - \psi_0; \quad |\Delta\psi_k| \ll 1.$$

Expanding integrand of expression (4) in the vicinity of the lower limit, we obtain

$$h = \sqrt{\frac{\Delta\psi_2}{8B_0}}; \quad B_0 = -\sum \lambda_i e^{-z_i \psi_0}. \quad (20)$$

Within the framework of this approximation, equation (17) acquires the form

$$\varepsilon_s B_0 \Delta\psi_2 = \varepsilon_g B_1 \Delta\psi_1^2, \quad (21)$$

$$B_1 = \sum \frac{v_i \mu_i z_i^2}{(1 + \mu_i)^2}, \quad \mu_i = \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_D}.$$

[When expanding right-hand part of equation (17), the term linearly dependent on  $\Delta\psi_1$  vanishes, in view of equation (15).]

Substituting equation (20) into (21), we obtain

$$\Delta\psi_1 = B_0 h \sqrt{\frac{8\varepsilon_s}{\varepsilon_g B_1}}; \quad \Delta\psi_2 = 8B_0 h^2. \quad (22)$$

Hence, at  $h \rightarrow 0$  inequality  $|\Delta\psi_1| \gg |\Delta\psi_2|$  is valid and virtually the entire potential difference is concentrated inside of the gel; ignoring the terms of the order of  $O(h^2)$ , we finally get

$$\psi_0 = \psi_D - B_0 h \sqrt{\frac{8\varepsilon_s}{\varepsilon_g B_1}}. \quad (23)$$

Calculating  $B_0$  from formula (20), we may substitute  $\psi_0$  for  $\psi_D$ . This substitution results in an error of the order of  $O(h^2)$  in equation (23). The only limitation, while using equation (23), is that  $\psi_0$  should not be too low since at  $|\psi_0| = 0$   $B_0$  vanishes, and formula (20) should be modified. In this case, the Debye approximation should be employed.

### THE DEBYE APPROXIMATION

Potential in the system studied is monotonically varied from  $\psi_0$  to  $\psi_D$ . Therefore, if

$$|\psi_D| \ll 1, \quad (24)$$

then the potential at any point of a system will be low in absolute magnitude. Using this fact, one may readily determine integral (14) as

$$\psi_h = \psi_0 \cosh h \quad (25)$$

and calculate the Donnan potential using equation (15):

$$\psi_D = B_2/B_3; \quad \xi_i = \frac{C_i}{Q_i} e^{-\Phi_i}; \quad (26)$$

$$B_2 = \sum \frac{v_i \xi_i z_i}{1 + \xi_i}; \quad B_3 = \sum \frac{v_i \xi_i^2 z_i^2}{(1 + \xi_i)^2}.$$

Expanding equation (17) into a series by the powers of entering potentials [with accuracy up to  $O(h^2)$ ], and making use of equations (25) and (26), we obtain the following quadratic equation for  $\psi_h$ :

$$B_4 \psi_h^2 = \psi_h^2 (\psi_D - 1) - 2\psi_h \psi_D + \psi_D^2 (3 - \psi_D), \quad (27)$$

$$B_4 = \frac{2\varepsilon_s \tanh^2 h}{\varepsilon_g B_3},$$

with only the smaller value of the square root having physical meaning

$$\psi_h = -\psi_D \frac{1 - \sqrt{4 + 3B_4}}{1 + B_4}, \quad (28)$$

because only this root fits the condition  $\psi_h \rightarrow \psi_D$  at  $h \rightarrow 0$ .

### APPLICABILITY LIMITS OF THE APPROXIMATE FORMULAS

Problems of the applicability limits for the two approaches discussed above have been specially treated in [8]. It was established that for 1:1 electrolyte it may be assumed (with 10% relative error) that an approximation of a small potential difference is valid at  $h \leq 0.45$ , with the Debye approximation at  $|\psi_D| \leq 0.57$ . We believe that these estimations may be taken as reference points, even in more complicated cases than those treated in [8].

### DEGENERATION

Analyzing the expression (10) for the concentration of the adsorbed ions, we may note that this expression is readily degenerated, i.e., it becomes more simple in the sense that its dependence on some input parameters ceases to exist. Then, the key value is

$$\chi_i = \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi}. \quad (29)$$

It may be recognized that, in a nontrivial way, expression (10) is affected by all entering parameters only at

$$0.1 \leq \chi_i \leq 10. \quad (30)$$

At

$$\chi_i \leq 0.1, \quad (31)$$

coverage of the active sites is so small that the role of coverage may be neglected (the Henry limit) and

$$A_i = C_i e^{-\Phi_i - z_i \psi}. \quad (32)$$

As can be seen, in this limiting case the dependence on  $Q_i$  disappears. In the opposite case, at

$$\chi_i \geq 10, \quad (33)$$

coverage of the sites is close to unity (the saturation limit) and, hence, coverage becomes constant. Then

$$A_i = Q_i, \quad (34)$$



that is, dependence on  $C_i$ ,  $\Phi_i$ ,  $z_i$ , and  $\psi$  ceases to exist.

The narrower the experimental range of parameters, the higher the probability that a part of the ions will be susceptible to degeneration. In this case, the restoration of a set of parameters from experimental data is strongly complicated due to the fact that we are trying to evaluate a larger number of parameters than are actually involved in the problem. Degeneration leads to increasing dispersion of the evaluation of the mostly degenerated parameter, and of all other parameters correlating with that parameter, because a larger number of parameters is responsible for the same bulk of information. Multivariate algorithms, including those involved in the analysis of the significance of all estimated parameters, should be employed in order to obtain the most reliable estimations.

### SIMPLE PARTICULAR CASE

All of the calculations performed are valid in the case of an arbitrary  $N$ -component solution which is characterized by  $2 + 2N$  parameters. To get better understanding of some features of our problem, consider the particular case of a 1:1 binary electrolyte. In this case,

$$z_1 = +1, z_2 = -1, C_1 = C_2 = C, \lambda_1 = +0.5, \lambda_2 = -0.5.$$

For further simplification, assume that ion 2 is inert ( $\Phi = 0$ ) and ion 1 is potential-determining ( $\Phi_1 < 0$ ,  $|\Phi_1| \gg 1$ ). Then equation (15) for the Donnan potential will be converted to

$$\frac{e^{-\Phi_1 - \psi_D}}{1 + \frac{C}{Q_1} e^{-\Phi_1 - \psi_D}} = \frac{e^{\psi_D}}{1 + \frac{C}{Q_2} e^{\psi_D}}, \quad (35)$$

with

$$\psi_D = -\Phi_1/2 + \ln(\sqrt{1 + q^2} + q), \quad (36)$$

$$q = \frac{C(Q_1 - Q_2)}{2Q_1 Q_2} e^{-\Phi_1/2}.$$

Even this example [equation (36)] demonstrates the degeneration of the problem: i.e., the dependence of  $\psi_D$

on a combination of  $Q_1$  and  $Q_2$  rather than on  $Q_1$  and  $Q_2$ , separately.

At  $Q_1 = Q_2$  (the density of the adsorption sites is the same for both types of ions),

$$\psi_D = -\Phi_1/2 \quad (37)$$

at any electrolyte concentration. The same situation will be observed at any values of  $Q_1$  and  $Q_2$ , when the electrolyte concentration is sufficiently low (the Henry limit,  $q \ll 1$ ). Under saturation at sufficiently high electrolyte concentration,

$$\psi_D = -\Phi_1 + \ln(C/Q_2); \quad Q_2 \ll Q_1, \quad (38)$$

$$\psi_D = \ln(Q_1/C); \quad Q_2 \gg Q_1. \quad (39)$$

In either case, the degeneration "takes up" one or two parameters. When  $Q_1 \neq Q_2$ , it is especially difficult to determine the larger value against the background of the smaller.

When  $Q_1 = Q_2$ , formula (23) is simplified to

$$\psi_D = -\Phi_1/2 + h \sinh(\Phi_1/2) e^{\Phi_1/4} \left(1 + \frac{C}{Q_1} e^{-\Phi_1/2}\right) \sqrt{\frac{8\epsilon_s}{\epsilon_g}}. \quad (40)$$

Figure 2 shows a few plots calculated by equation (36), illustrating the dependence of the Donnan potential on concentration. At  $Q_1 \neq Q_2$ , each curve plotted in semilogarithmic coordinates may be distinctly divided into three regions: two straight lines corresponding to limiting cases (38) and (39), connected together by a narrow (smaller than one decimal order of magnitude) transition zone. When the adsorption potentials are low ( $\Phi_1 = -1$ , in Fig. 2), the position of the transition zone is determined as  $C = \min(Q_1, Q_2)$ . In Fig. 2, the degeneration is clearly visible, both at low and high concentrations [at  $Q_2 = 10Q_1$  and  $C > 10^{-4}$  mol/l, the curves for  $\psi_D$  coincide irrespective of  $\Phi_1$ , due to condition (39)].

Figures 3a and 3b demonstrate data calculated by formula (40) for  $\epsilon_g = 15$ . At very low concentrations, the disjoining pressure is small due to the very low content of ions in the system [see formula (1)]. When the concentration is raised, pressure first increases (the ascending part of the curve in Figs. 3a and 3b), and then starts to reduce rapidly due to a decrease in the overlapping of the electrical double layers, and a sharp decrease in  $\psi_0$ . This is qualitatively consistent with the pattern of the disjoining pressure for the model of a smooth surface with constant surface potential.

Differences in these models can be followed with the help of the Debye approximation (Fig. 4,  $Q_1 = Q_2$ ,  $\epsilon_g = 15$ ). In this figure both surfaces are characterized by a constant potential equal to the Donnan potential of the gel. As a result, both models appear to be alike, provided that  $C < Q_1$ . In the case of a smooth surface, the potential in the middle of the interlayer reduces solely

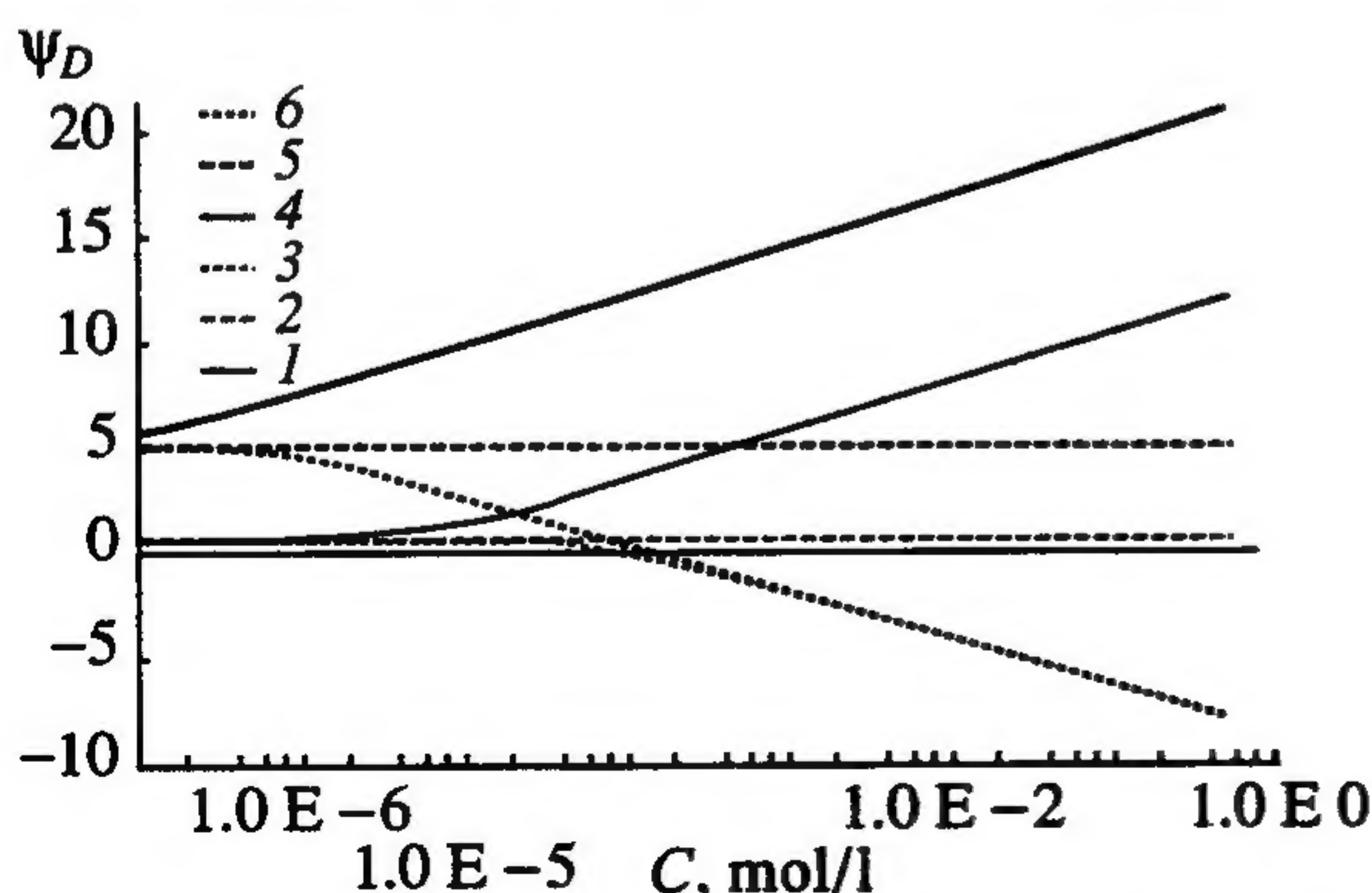


Fig. 2. Dependence of the Donnan potential of the gel layer on the electrolyte concentration ( $Q_1 = 10^{-4}$ ): (1 - 3)  $\Phi_1 = -1$ , (4 - 6)  $\Phi_1 = -10$ ; (1, 4)  $Q_2 = Q_1/10$ , (2, 5)  $Q_2 = Q_1$ , (3, 6)  $Q_2 = 10Q_1$ .



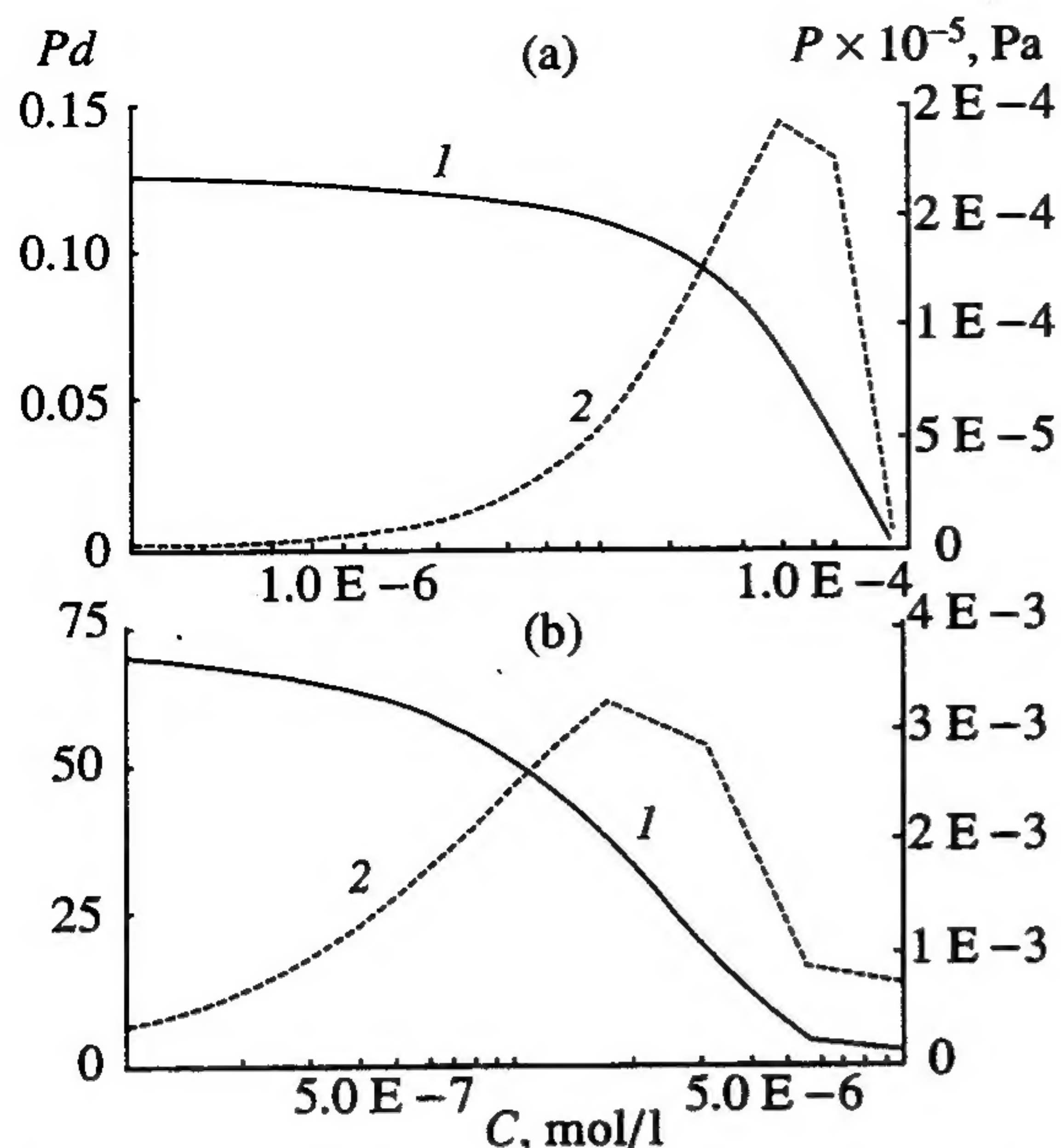


Fig. 3. Dependence of the disjoining pressure between two gel layers on the electrolyte concentration, calculated in the approximation of low potential difference using equation (40):  $Q_1 = Q_2 = 10^{-4}$  mol/l; clearance width ( $X_A$ ) = 20 Å; (1) dimensionless pressure (on the left-hand axis  $Y$ ), (2) pressure, in Pa (on the right-hand axis  $Y$ ); (a)  $\Phi_1 = -1$ , (b)  $\Phi_1 = -10$ , (1) dimensionless pressure, Pa, (2) pressure  $P$ , in atm.

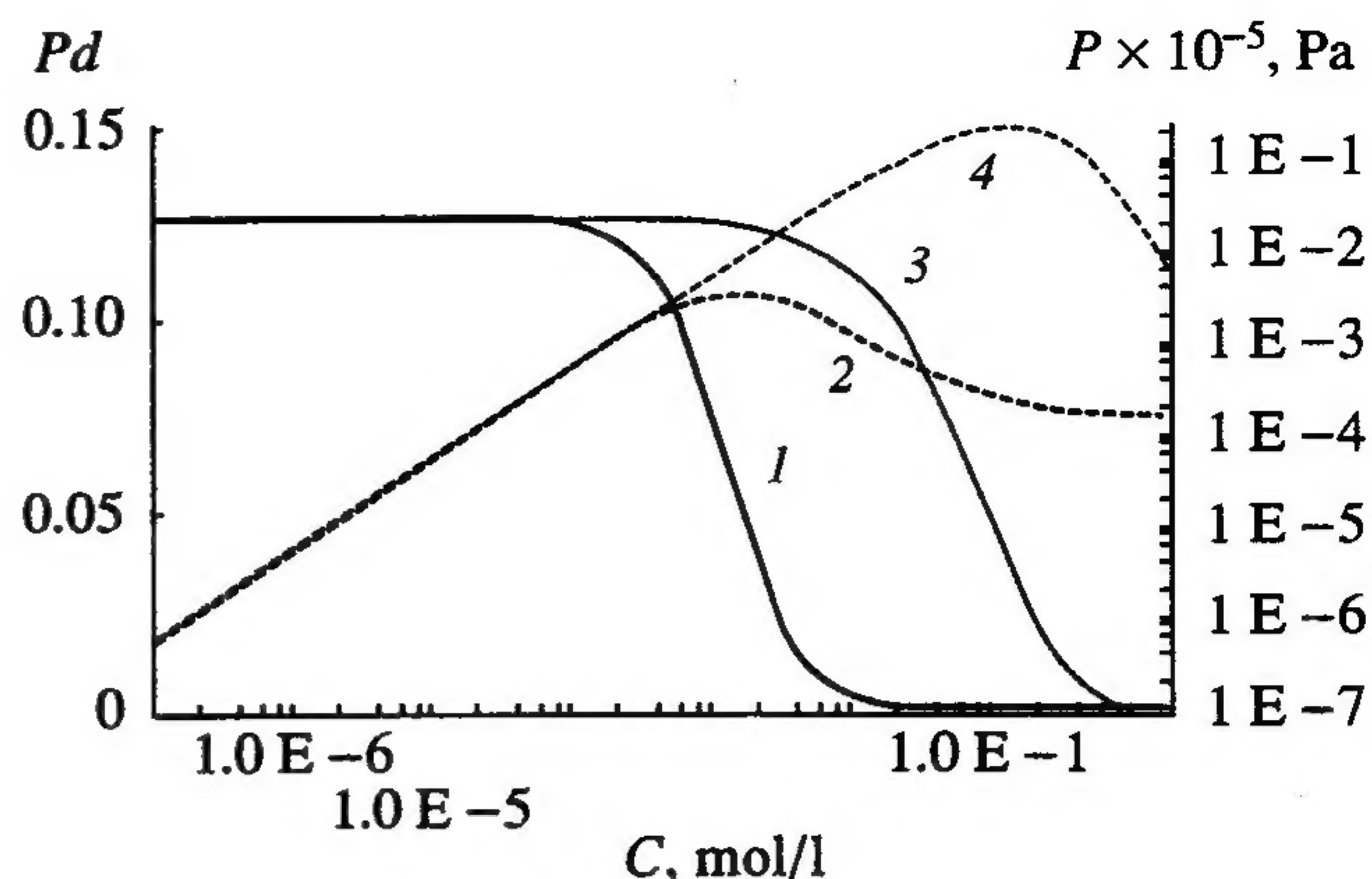


Fig. 4. Dependence of the disjoining pressure between two gel layers on electrolyte concentration, calculated in the Debye approximation by equation (36): (1, 3) dimensionless pressure (on the left-hand axis  $Y$ ), (2, 4) pressure, in Pa (on the right-hand axis  $Y$ ); (1, 2) gel layer model, (3, 4) smooth surface model; (1) dimensionless pressure  $P$ , (2) pressure  $P$ , in atm.  $Q_1 = Q_2 = 10^{-4}$  mol/l; clearance width ( $X_A$ ) = 20 Å;  $\Phi_1 = -1$ .

due to the decrease in thickness of the electrical double layer, whereas in the case of gel layers, rearrangement of the potential between gel and solution, accelerating the reduction of the potential with increasing concentration, is also important (in addition to this first factor). This circumstance is revealed by the fact that the steepness of the descending part of the curve for dimensionless disjoining pressure is higher for the gel layer and lower for the smooth surface. When capacity  $Q_1$  is increased, curve 1 for the gel layer shifts to the top right of the curve until it coincides with curve 3. With increasing interlayer thickness, curve 3 shifts to the left, whereas the slope of the curve 1 (in addition to the shift to the left) decreases until both curves will merge again into one curve. At low potentials, the disjoining pressure of gel layers will always be lower than pressure of smooth surfaces, with the  $\zeta$ -potential equal to the Donnan potential of gel layers. Conversely, the disjoining pressure of gel layers will always be higher than that for smooth surfaces, with the  $\zeta$ -potential equal to  $\zeta$ -potential of the isolated gel layer.

## CONCLUSION

The main parameter controlling the electrostatic component of the disjoining pressure of the particles covered with the gel layer is the Donnan potential of the gel. This value is beyond the reach of direct measurement. However, it may be calculated by complex electrosurface measurements, including the detection of the surface charge by titration and the measurement of sur-

face electrical conductivity. When the Donnan potential is replaced by the  $\zeta$ -potential, which can be measured directly using electrophoresis, significant error may arise during the calculation of the disjoining pressure. This circumstance is very important when studying biological cells, where molecular attractive forces are low and, hence, where small variations in electrostatic repulsive forces may dramatically change the total force balance.

Three approximate methods, employed to receive analytical results, may be applied both to the case of independent adsorption (which was treated in this paper) and to that of competitive adsorption. These include expansion over the small potential difference, the Debye approximation, and the approximation of the thin double layer (see Appendix).

Any variant of the description of the fixed charge of colloidal particles by means of the Stern–Langmuir isotherms involves a large number of parameters. Theoretical formulas used to estimate these parameters from experimental data are susceptible to degeneration, and thus, parts of these parameters defy possible estimation. This difficulty may be overcome by using ideas of experimental design.

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## APPENDIX

### Case of a Larger Width of Interlayer

When  $h \rightarrow \infty$ , the potential in the interlayer center tends to zero. We denote

$$\psi_f = \psi_h|_{h \rightarrow \infty}; \quad \Delta\psi_3 = \psi_f - \psi_h, \quad (\text{A1})$$

where  $\psi_f$  is the potential of the gel-solution interface for a single gel layer.  $\psi_f$ -Potential fits the equation resulting from (17):

$$\begin{aligned} & \varepsilon_s \sum \frac{\lambda_i}{z_i} (e^{-z_i \psi_f} - 1) \\ &= \varepsilon_g \sum v_i \ln \left[ \frac{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_f}}{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_D}} \right]. \end{aligned} \quad (\text{A2})$$

Expanding (17) over powers of small values of  $\psi_0$  and  $\Delta\psi_3$ , and with regard for (A2) we obtain

$$\varepsilon_s (\Delta\psi_3^2 - \psi_0^2) / 2 = \Delta\psi_3 \varepsilon_g \sum \frac{v_i z_i \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_f}}{1 + \frac{C_i}{Q_i} e^{-\Phi_i - z_i \psi_f}}.$$

As can be seen from this equation,  $\Delta\psi_3 \sim O(\psi_0^2)$ , i.e., at very slight overlapping of the electrical double layers in the interlayer, the potential of the gel surface varies negligibly in comparison to that in the interlayer center.

Hence, with good accuracy one may calculate  $\psi_0$  from equation (14), substituting  $\psi_h$  for  $\psi_f$ :

$$h = \int_{\psi_0}^{\psi_f} \frac{d\psi}{\sqrt{2 \left[ \sum \frac{\lambda_i}{z_i} (e^{-z_i \psi} - 1) - \frac{\psi_0^2}{2} \right]}}. \quad (\text{A3})$$

Here, the simplification is that the system of equations (14) and (17) is decomposed into two independent equations: equation (A2) to determine  $\psi_f$  and equation (A3) to determine  $\psi_0$ .

According to [8], this approximation is valid at an error level of 10%.

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